Final Report

STUDY OF A MULTIPLE RESERVE ELECTROCHEMICAL
POWER SOURCE

Prepared for
Chief, Solar and Chemical Power Systems
National Aeronautics and Space Administration
NASA Headquarters
Washington, D. C.   20546
Attention: Ernst Cohn, OART, Code RNW

Contract NAS7-672

EOS Report 4008-Final   8 November 1968

Prepared by
A. Thompkins
M. Klein

Approved by

K. Winsor (signature)

K. Winsor, Manager
Power Systems Department

CONTENTS

ILLUSTRATIONS

SECTION 1

CONCLUSIONS AND RECOMMENDATIONS

A four-month study program was carried out which included limited experimental work to determine the feasibility of metal oxygen primary batteries for multiple reserve use. Cadmium, iron, and magnesium anodes were evaluated coupled with oxygen. The concept consists of a series-connected monoblock that contains the anode, electrolyte, oxygen electrode, and a gas-fed manifold. When power is required, oxygen from a lightweight high-pressure storage vessel is fed through a pressure reduction regulator to the monoblock. In periods of nonuse, the oxygen source is closed and the battery remains in the ready condition.

The cadmium-oxygen system presented the following positive advantages: ease of cadmium plate construction, the capability of a feasible on/off power control, the stability of cadmium in KOH electrolyte, and the ease of plate formation. Plate construction simply involves pressing a mixture of cadmium oxide and silver powder into an electrode sheet. To form the cadmium into an electrically active plate requires only charging in KOH over a period of time. An on/off power control can be effected by merely supplying oxygen to the system and cutting off the oxygen. The sponge cadmium appears stable and is not adversely affected in KOH electrolyte. From tests conducted in this program, 5 to 10% capacity loss was observed in one month storage at room temperature. However, these cells were not well sealed. Other wet stand tests on silver cadmium and mercury cadmium cells show good capacity retention for years. Typical discharge of single cells yielded 0.9 volts. Engineering analysis of complete battery systems shows that batteries in the 30 to 45 W-h/lb range should be attainable.

Although the magnesium-oxygen sytem operates at a higher voltage than the cadmium-oxygen system, and requires less material once electrolyte is added to a magnesium cell, self-discharge ensues.

Sodium chloride was used as the electrolyte in the test cells, and it was found to cause rapid self discharge. If the battery were used immediately after activation, engineering analysis shows that energy densities of 47 to 81 should be attainable.

Difficulties were encountered with the iron-oxygen system in preparing efficient iron electrodes. The experimental data indicate that unless the iron electrodes get complete protection from the outside air after the reduction process, the ensuing oxidation is detrimental to the electrode's effectiveness. The best electrodes fabricated achieved only 25% utilization. Due to the lack of a good base line and test data no engineering analysis was conducted on this system. However, if an efficient electrode were achieved, the resultant batteries would probably have energy densities between the Cd and Mg systems.

From the results obtained, a number of areas requiring further investigations can be defined to complete the development of the multiple reserve metal-oxygen batteries. Sufficient information and analysis has been generated to justify a continued effort. In the case of cadmium oxygen, additional studies should be undertaken on improving the cadmium electrode utilization, and on obtaining more parametric data on electrode porosity, electrode thickness, operating current density, and intermediate duty cycles. American Cyanamid oxygen electrodes were used in all of the evaluations undertaken in this program. Studies should be conducted to evaluate other types of oxygen electrodes for reduced costs and improvements in performance. Also, it will be necessary to build a large number of test cells and subject them to various storage conditions and intermediate duty cycles to obtain the necessary data on capacity retention. With the completion of these

tasks, a complete monoblock battery with a lightweight storage tank should be built to demonstrate the total battery capabilities.

It would also be possible to pursue the magnesium-oxygen couple. In this area, extensive efforts are required to achieve a different salt electrolyte than that used in these studies. The electrolyte should be capable of supporting a reasonable current density on an oxygen electrode, and there should be little corrosion of the magnesium during wet stand. With the achievement of such an electrolyte, the system optimizations could be conducted, and complete batteries could be built and subjected to testing. The achievement of a compatible oxygen electrode electrolyte, magnesium anode, wet system would enable an increase in energy density yield of a multiple reserve battery by a factor of 2 or 3 over that achieved by cadmium oxygen. To make the iron system practical, it would be necessary to develop an electrode that is capable of good utilization. This would involve the evaluation of various types of electrode fabrication approaches and the accompanying electrical testing.

SECTION 2

INTRODUCTION

This final report reviews the progress made on the development of a multiple reserve electrochemical power source under NASA Contract NAS7-672 over the period of May 1968 to August 1968. The program objective was to study the applicability of metal-gas systems of cadmium-oxygen, magnesium-oxygen, and iron-oxygen for multiple reserve use.

Many space applications require intermittent use of a battery with long periods of dormancy where no power is required. Thus, it would be desirable to have a primary battery that could be partially discharged, allowed to sit without deterioration, and subsequently reused. Due to the nature of existing primary batteries, gradual deterioration is encountered during wet shelf life and those systems that have relatively good wet shelf capabilities have a low energy yield. (Reserve activated primary batteries have been developed for one-shot applications where long periods of shelf life are required; the battery is used soon after activation.)

The justification for any of these reserve primary systems is that they permit the use of a high-energy electrochemical system that generally would not meet the shelf life requirements of the application. The multiple reserve concept is just an extension of this criteria. Ideally, the primary battery should be capable of partial discharges with long periods of dormancy without any self discharge.

This program was undertaken to evaluate a system consisting of a metallic anode, oxygen electrode, and electrolyte which are contained within a monoblock with a manifold gas feed system. When the battery is to be discharged, oxygen gas from a separate high-pressure storage tank is fed to the monoblock.

In periods of dormancy, the oxygen feed is closed and the wet monoblock remains inert. In order for the system to be practical, the anode-oxygen-electrode combination must be stable in the electrolyte. Furthermore, the combined weight of the oxygen plus its storage vessel, auxiliary hardware, and the battery block must result in a system that has an attractive energy density.

SECTION 3

TECHNICAL DISCUSSION

3.1 METAL-OXYGEN MULTIPLE RESERVE SYSTEM CONCEPT

The metal-oxygen primary battery offers promise for multiple reserve applications. It is based on the use of an anode-electrolyte-oxygen electrode stack which is fed oxygen when the battery is to be operated. To make such a system work, the anode-cathode arrangement has to be stable in the electrolyte and have sufficient shelf life.

Figure 1 shows a schematic of the metal-gas concept utilizing oxygen as the gas. It consists of the following: a multicell, series-connected monoblock which contains the anode, electrolyte and cathode; a manifold system to feed oxygen to the individual cells; and a separate oxygen storage container with a pressure regulator and an on/off valve. The system is a sealed arrangement that requires only the opening of the oxygen gas valve to enable electrical power to be drawn from the stack. The regulator is set at some relatively low pressure (5 to 20 psi) so that the battery block would not have to withstand high pressure. The oxygen storage tank would have pressures up to 3000 psi for good compact storage.

3.2 METAL-OXYGEN SYSTEM

Utilizing the package concept described in the previous section, it is possible to build a variety of metal anode-oxygen systems that are of interest for multiple reserve applications. Table I lists the anodes that were considered for the battery.
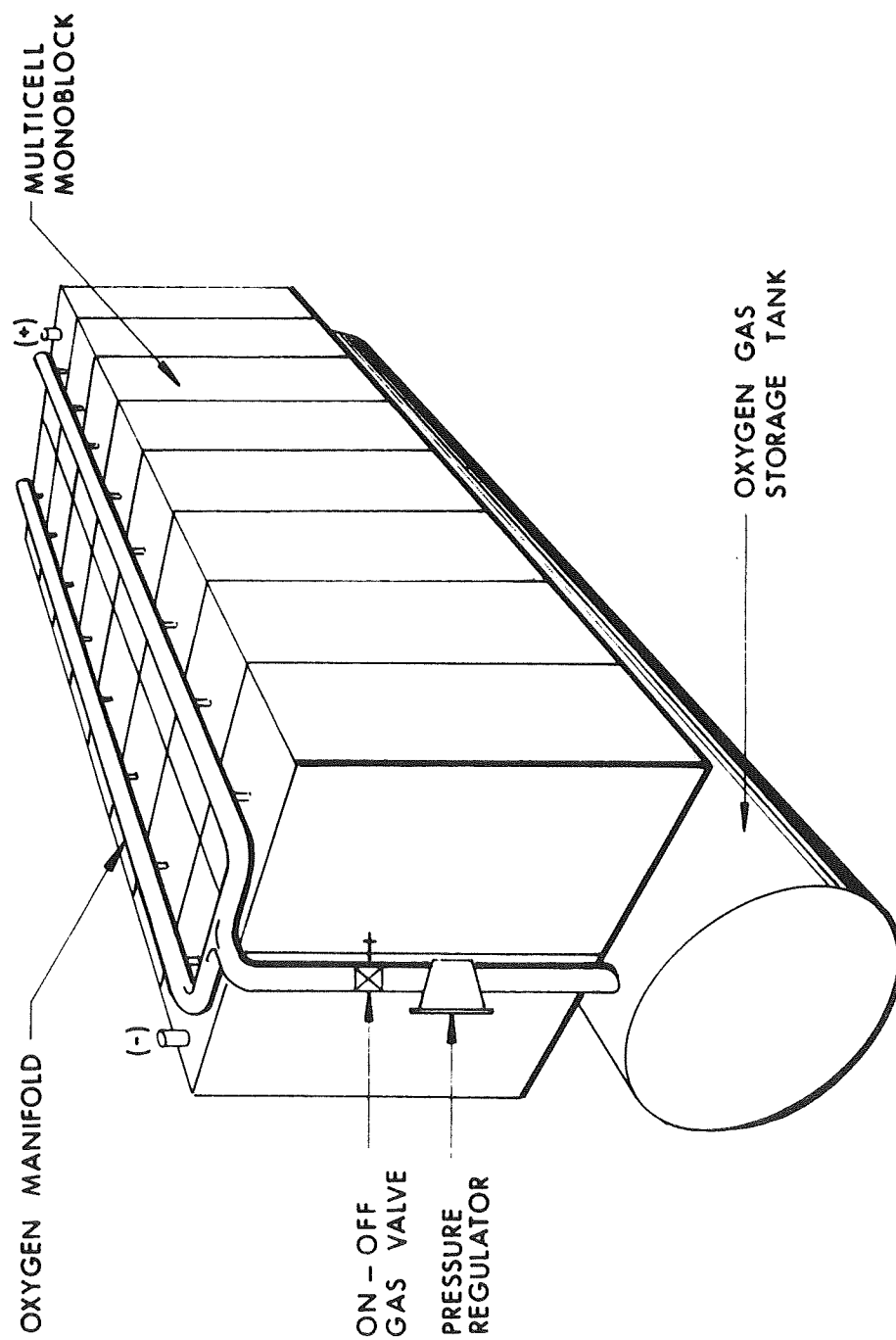
Figure 1. Multiple Reserve Metal-Oxygen Primary Battery

MULTICELL MONOBLOCK

OXYGEN GAS STORAGE TANK

OXYGEN MANIFOLD

ON – OFF GAS VALVE

PRESSURE REGULATOR

TABLE I

ANODIC METALS, THERMODYNAMIC CHARACTERISTICS

Anode	Weight	gm/A-h	E_O Anode	E_O Cell	W-h/lb with O_2	Operating Cell Voltage
Mg	24.31	0.45	2.69	3.091	1800	1.50
Fe	55.85	1.04	0.877	1.278	432	0.95
Cd	112.41	2.10	0.809	1.210	228	0.90

Since the concept is based on having the anode in contact with the electrolyte, it is important to consider the stability of the anode electrolyte systems. A cadmium or iron system would employ a potassium hydroxide electrolyte. Based on prior experience, cadmium is quite stable in potassium hydroxide, and capacity retention for many years can be projected. Iron has been used in nickel-iron batteries with substantial success. However, these batteries are usually floated to maintain capacity retention of the iron electrode. Magnesium reacts rapidly in acid electrolyte and passivates in an alkaline electrolyte; therefore, it is necessary to use a neutral salt electrolyte. The best electrolyte for magnesium batteries has been found to be magnesium perchlorate. However, the oxygen electrode performs very poorly in this electrolyte and the most compatible oxygen systems consist of magnesium chloride, magnesium bromide, or sodium chloride salt electrolytes. The charge retention of magnesium in these salts varies, and can be improved by the addition of chromate inhibitors. Therefore, the choice of anode naturally will have a substantial effect on the energy density of the complete battery and the total wet life. A family of batteries with different energy density and wet shelf life capability, which can be custom designed for a particular application, is possible.

The theoretical W-h/lb values do not take into consideration the water consumed in the reaction; the values for iron were based on a two-electron transfer per atom with the end product being Fe $(OH)_2$. In actual practice, a mixed oxide of iron is probably formed, but this basis is good enough for comparative purposes.

3.3 SINGLE CELL CONCEPT

In metal-oxygen and fuel cell batteries that require a gas electrode reaction, it is necessary to provide gas access to the reacting surface. Previous work conducted in this area revolves around the use of either a liquid electrolyte with a wet-proof-type electrode or a system of electrolyte trapped in a capillary matrix to prevent flooding of the electrode. The liquid system is precarious and is subject to deterioration with life. The capillary system is electrolyte-limited and also makes the device relatively sensitive. Based on prior activities at EOS, a compromise between these two approaches was pursued in this program, and it proved quite applicable to a multiple reserve primary battery. The concept consists of a flooded capillary approach in which the electrodes are spaced with a capillary matrix, and a small reservoir of electrolyte exists within the cell. This concept is employed in most battery systems of a special-purpose type such as silver-zinc, nickel-cadmium, silver-cadmium, etc.

Figure 2 illustrates the construction of the electrode stack. It consists of the conventional parallel electrode hookup, with gas access to the back side of the oxygen electrodes through a diffusion screen which is open to the stack edge. Naturally, the key to minimizing self-discharge in any of the metal-oxygen systems is to prevent oxygen access to the metallic anode. This is accomplished by keeping the matrix in contact with the anode relatively wet and providing an edge seal to prevent oxygen leakage to the side of the anode. The edge seal
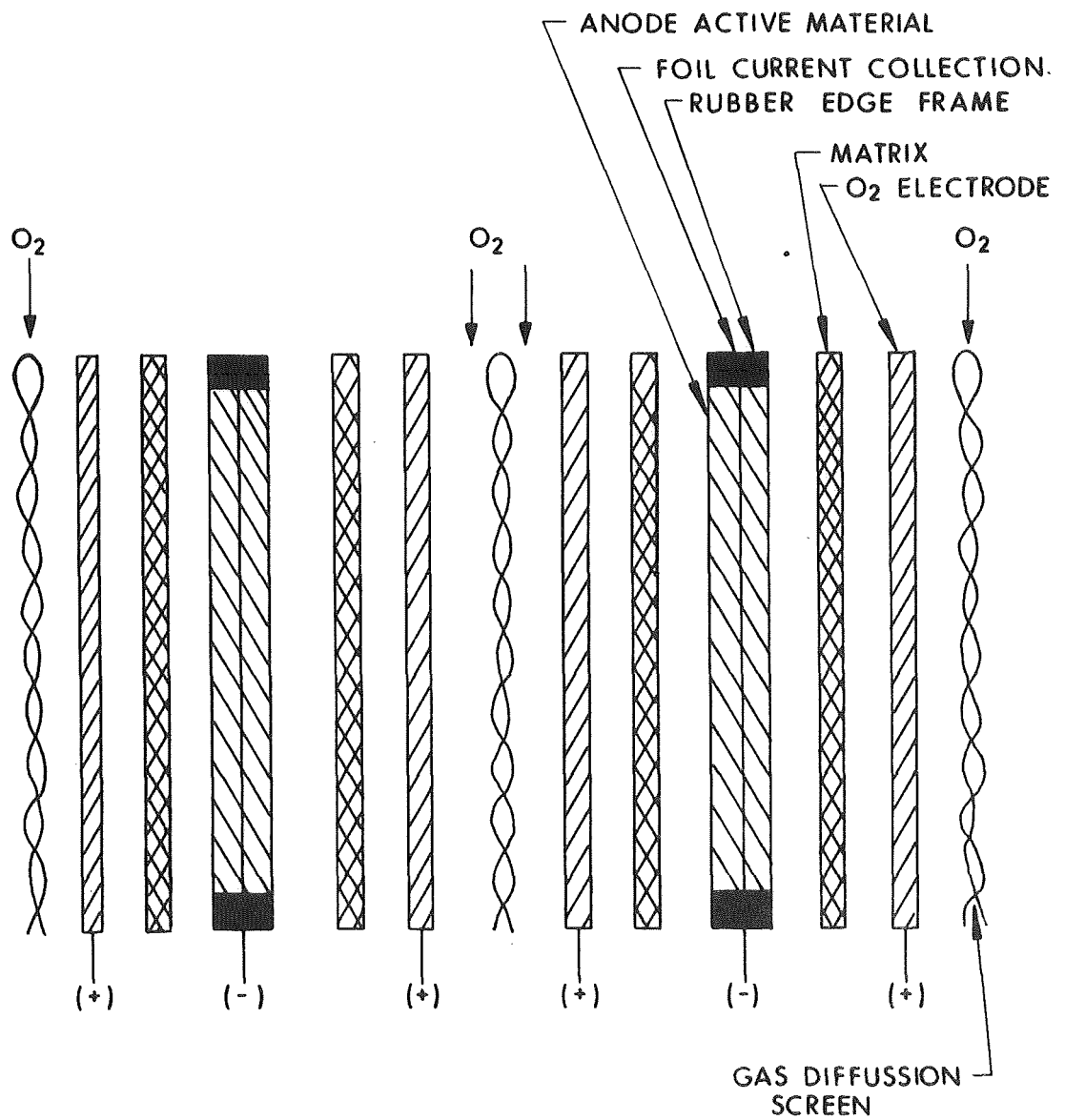
Figure 2. Metal-Oxygen Electrode Stack

is accomplished by utilizing a metal foil as the anode current collector, bonding the collector edge with a rubber frame, and placing the active anode in this frame. By this technique, the anode is totally enclosed and not subject to reaction with oxygen. Figure 3 shows a photograph of the Cd-O_2 stack components. Such a cell is fabricated with an electrolyte quantity slightly more than that absorbed by the anode matrix arrangement, providing a small pool of electrolyte in the bottom of the cell which acts as a reservoir for the cell reaction.

Figure 4 shows the single cell case design with attached manifold section. By fabricating this self-contained cell in its own plastic container, as is done in many other battery systems, the probability of intercell electrolyte leakage and self-discharge (which would be very detrimental in a long life primary battery) is avoided. The cells of this type are electrically connected in series and manifolded together to a common oxygen storage tank. Provision can readily be made within the manifold between cells to prevent a liquid junction.

3.4 EXPERIMENTAL DATA

To serve as a base line for the design analysis and to demonstrate feasibility, a limited number of single cells were built utilizing the concept as shown in Fig. 2. Arbitrarily, a 5 to 10 ampere-hour (A-h) capacity cell construction was selected to minimize costs and materials. These cells were subjected to electrical tests at different load levels and rates of discharge.

3.4.1 CADMIUM-OXYGEN TEST CELLS

The cadmium-oxygen tests conducted in the program employed a cell stack such as shown in Figs. 2 and 3. Oxygen electrodes employed throughout the program were the American Cyanamid AB-6 (9 mg Pt/cm^2) type electrode. The matrix employed was a 0.025-inch-thick potassium titanate
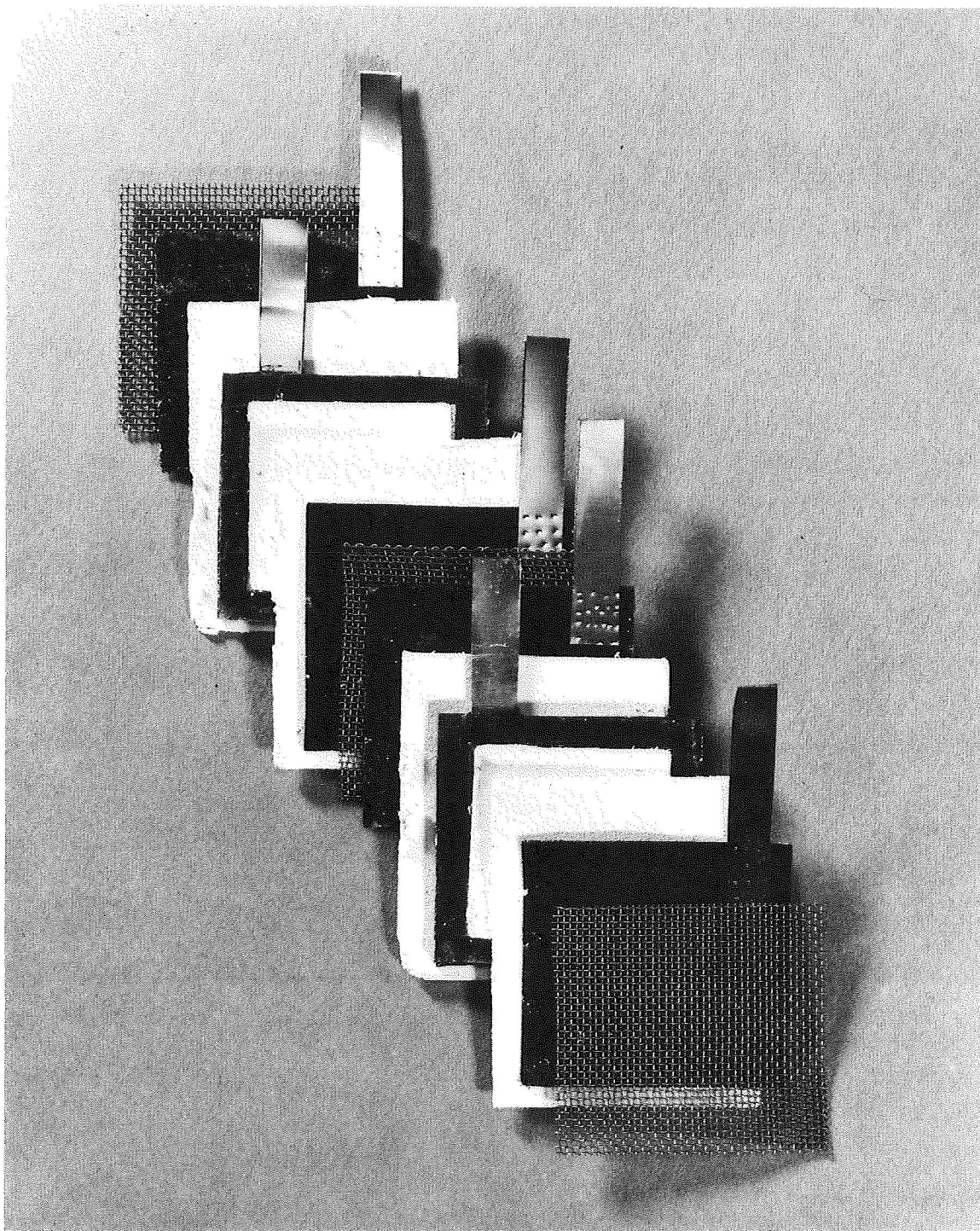
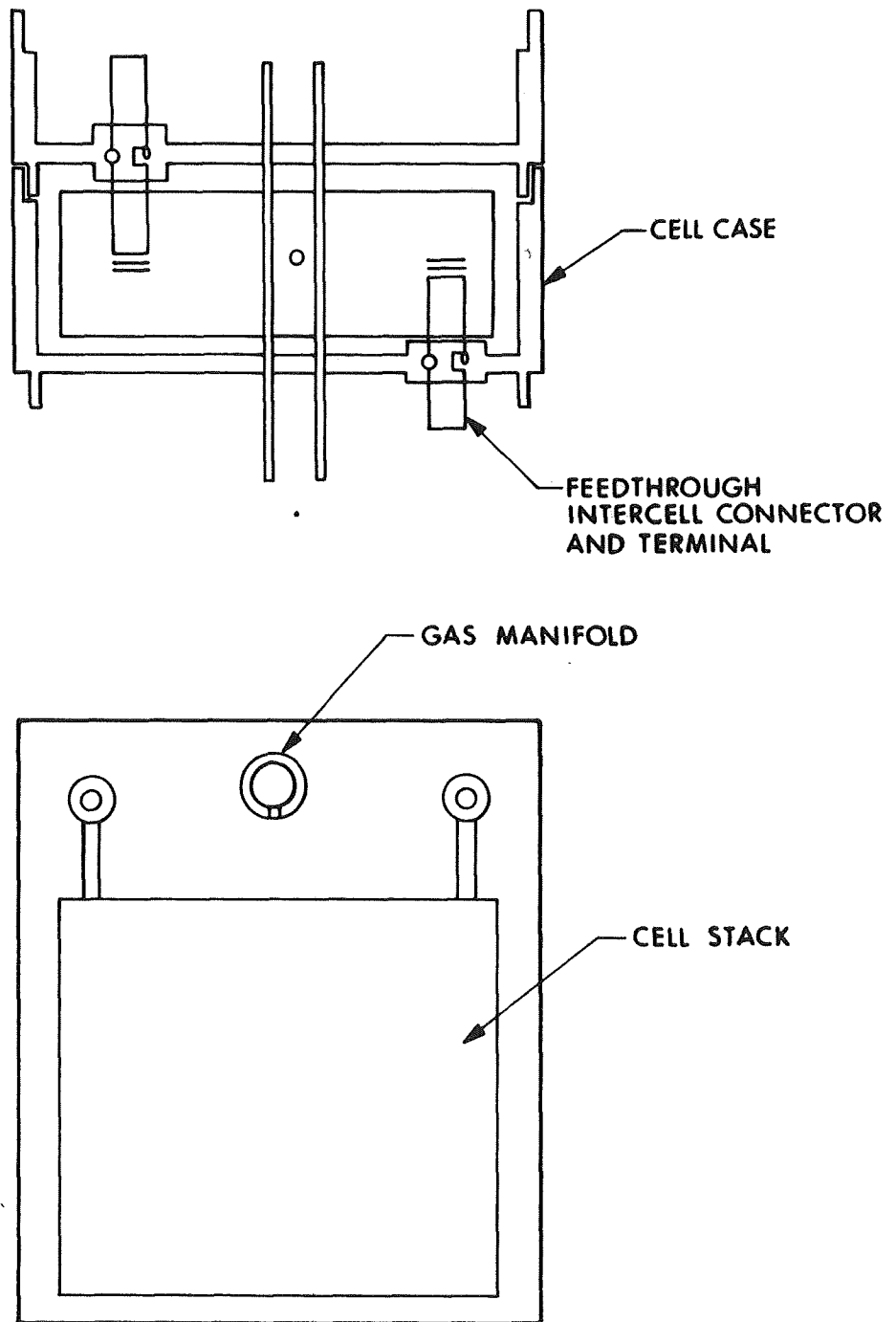Figure 3. Actual Electrode Stack Components

Figure 4.   Single Cell Design

composite developed at EOS for the hydrogen-oxygen fuel cell (Ref. 1).
This material has the desirable characteristics of low resistance in
KOH and good electrolyte absorption. It is inert in KOH in an oxygen
atmosphere over long periods of time, swells slightly upon wetting, and
when wet, acts as a good barrier against oxygen diffusion to the anode.
Nylon plastic screen (20 x 20 x 0.010 mesh) was employed for gas dif-
fusion purposes. The anodes were constructed of pressed cadmium oxide
with 5% to 10% silver powder. After pressing, the electrodes were
charged in KOH against nickel sheets in a charging cell. They were
then washed and dried in preparation for future cell construction.
Initially, cadmium-oxygen test cells (approximately eight A-h theo-
retical capacity) produced less than one A-h. The formation process
at this point consisted of charging to 200% of the theoretical capacity
at a rate of one ampere for 16 hours. From reference electrode checks,
it was determined that the cadmium electrode was causing the failure.
To establish a reference point for evaluating the cadmium electrodes,
nickel-cadmium battery combinations were built using cadmium test
plates. Commercial nickel plates were used as the counterelectrode
in quantities that would exceed the theoretical capacity of the cad-
mium; consequently, the limiting factor for the control combinations
was the cadmium. Using this technique, the initial nickel-cadmium
control combination yielded 3 ampere-hours. However, by reducing the
charge current from 1.0 ampere to 0.25 ampere, in conjunction with
extending the charge time, considerable improvements in utilization
were achieved. With the revised formation charging procedure, over
70% of the theoretical capacity was obtained from the cadmium test
plates versus commercial nickel electrodes.

Another change aiding the cadmium plate process was to place the pressed
cadmium oxide directly into the cadmium-oxygen cell and form it in place.
Originally, it was intended that the cell construction and assembly would
be a three-step process--cadmium formation, washing and drying of the

cadmium, and finally cell assembly. The wash-and-dry step of the
formation procedure was eliminated by charging in place. Although
the wash-and-dry step of the formation process has desirable merits
for the Multiple Reserve Program, more time and effort are needed to
develop the process to the point that it can be effectively included
in the cadmium plate formation procedure. The big asset to be gained
with the wash-and-dry process is storage for future activation.

After the plate capacity had been developed with the use of the nickel-
cadmium control combinations, similar plates were placed in test cells
with the American Cyanamid AB-6 oxygen electrodes. These battery com-
binations also yielded an ampere-hour capacity in excess of 70% of the
cadmium's theoretical capacity. A typical $Cd-O_2$ battery discharge mode
is shown in Fig. 5, and a polarization check is shown in Fig. 6.

After the establishment of a cell construction and design that was
capable of good initial performance, a limited investigation was carried
out to evaluate capacity retention. From other work, the cell compo-
nents of O_2 electrode, KT matrix, and sponge cadmium have all demon-
strated exceptional stability. AgO-Cd cells are capable of 70-80%
capacity retention for one year at room temperature and the loss is
probably due to the silver electrode (Ref. 2). Sponge cadmium elec-
trodes employed in HgO-Cd cells have demonstrated virtually no loss in
capacity after storage at 165°F for 4 months (Ref. 3). Therefore, it
can be expected that the cadmium electrode will perform equally well
in the $Cd-O_2$ system. The American Cyanamid oxygen electrode is made up
of Pt black and Teflon, and in capillary fuel cells it has operated for
thousands of hours. There is no reason to expect deterioration on wet
stand.

A limited number of cells were placed on wet shelf life stand to demon-
strate the capacity retention capabilities of the cadmium-oxygen system.
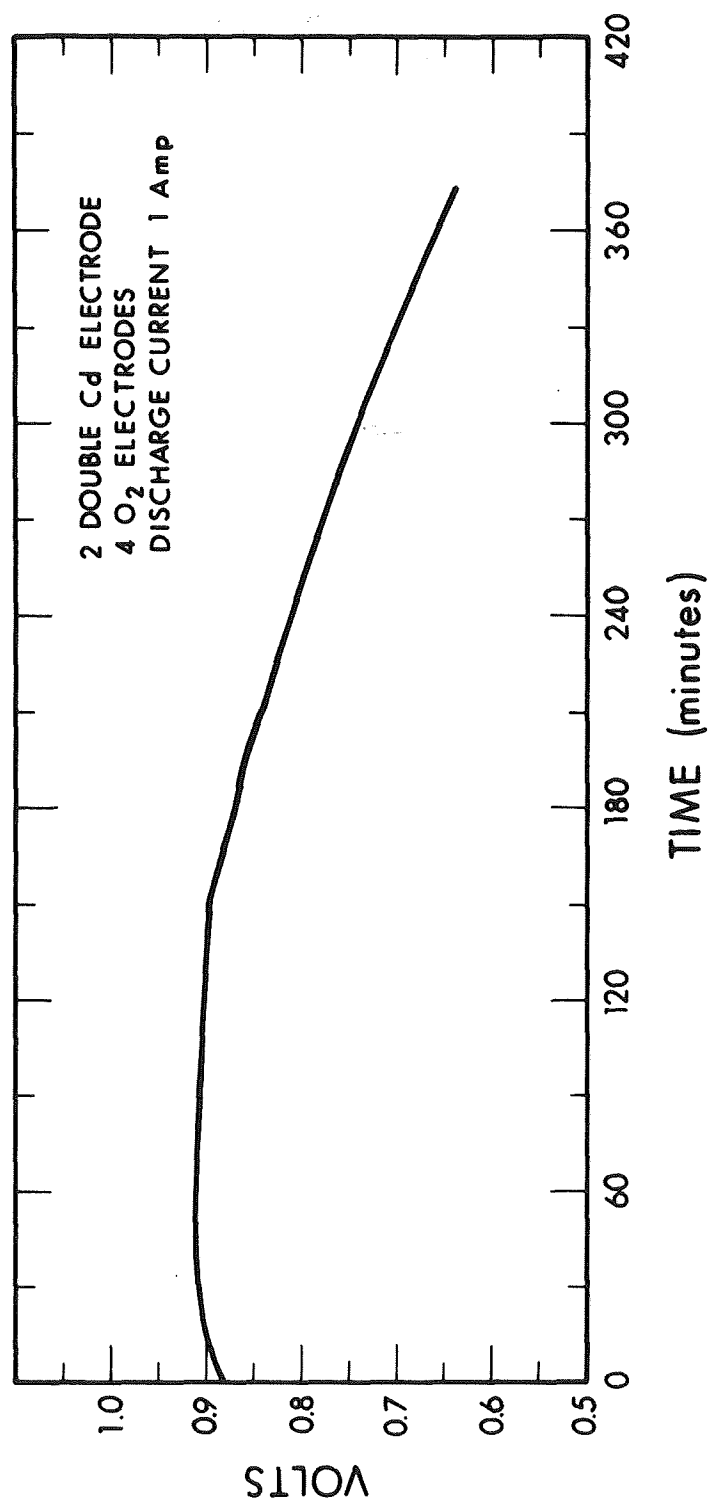Although the data from this tests are inclusive, the results indicated

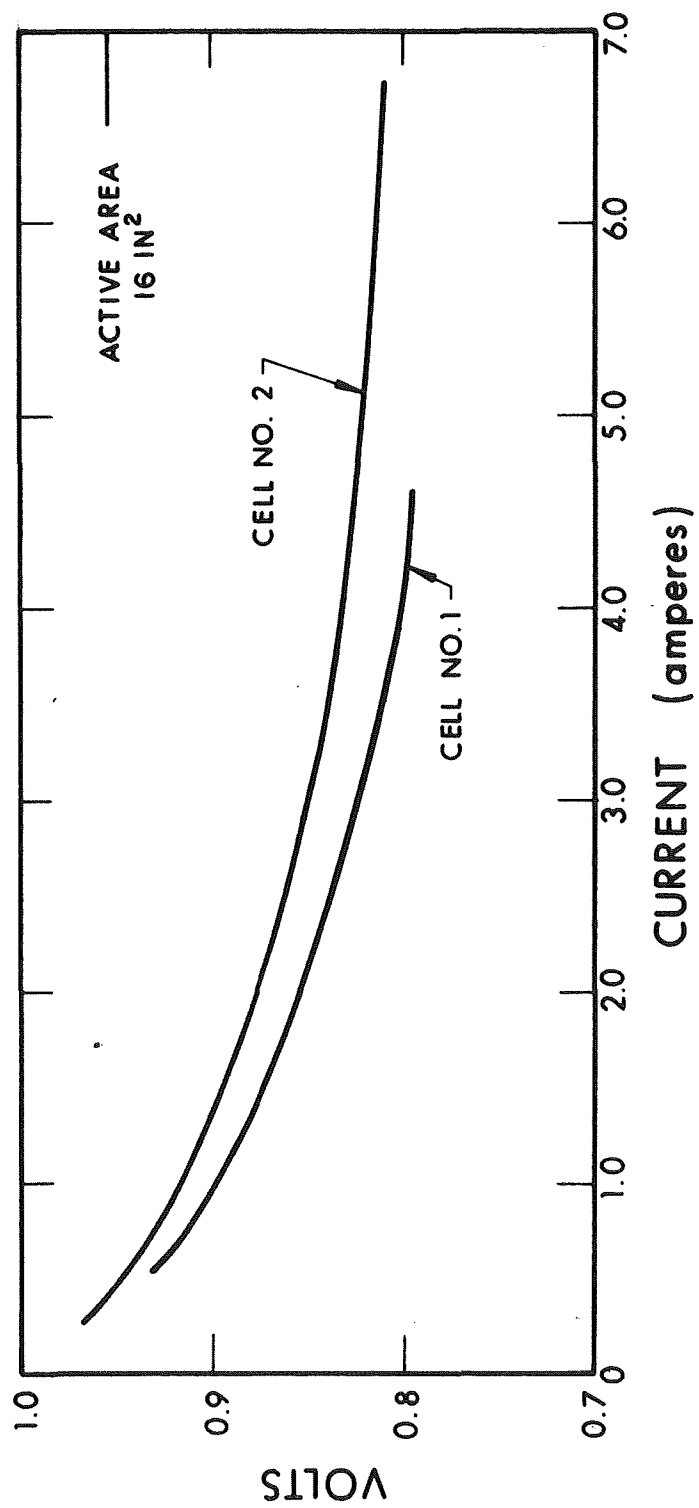Figure 5. Typical Cd-O$_2$ Battery Discharge Mode

Figure 6. Multiple Reserve Cadmium-Oxygen Polarization Curves

losses of capacity in the 5% to 10% range over a one-month storage period at room temperature. Three reasons for this loss are readily apparent. First, these cells were built before the advanced techniques of cell construction had been developed, the cells probably had a large capacity variation, and the cells also did not possess an adequate seal between the cell body and cell top.

The weight of a typical test cell (Fig. 4) came to a total of 132 gms. This cell has a theoretical capacity of 8 A-h. A complete breakdown of the test cell components is listed in Table II.

<div align="center">

TABLE II

SINGLE CELL WEIGHT ANALYSIS

</div>

(4) Cadmium electrodes - (0.030 inch x 2 inches x 2 inches)
CdO, silver powder .... 22.5 gm

(4) Oxygen electrodes, tabs (0.010 inch x 2.5 inches x 2.5 inches) .... 12.0 gm

(2) Current collector (0.002 inch x 2.5 inches x 2.5 inches) 10.0 gm
foil and rubber frame

(4) Separators (0.025 inch x 2.5 inches x 2.5 inches) ...... 9.0 gm

(2) Connectors, 2 screws, 2 washers, O-ring .... 11.0 gm

(3) Gas distribution screen .... 4.5 gm

                                                             69.0 gm

Electrolyte .... 30.0 gm

Plastic case 5/8 inch x 2 3/4 inches x 3 1/2 inches .... 33.0 gm

                                            Total   132.0 gm

3.4.2 MAGNESIUM-OXYGEN TEST CELLS

Investigative work was done with the magnesium-oxygen combination which involved testing two different magnesium alloys using a 10% NaCl electrolyte solution. The test cell construction was very similar to the one used for the Cd-O_2 couple which was schematically outlined in Fig. 2.

No current collector was needed for the magnesium because the metallic anode was cut from sheets of magnesium alloy and used with a separator and oxygen electrode to complete the couple.

The two alloys tested were the Dow AZ31B and the Melmag AZ61 with lead. Figure 7 shows polarization curves for the two different magnesium alloys and the indications are that the Melmag is the better performing alloy. Corrosion tests were run on two samples of each alloy. The rates of corrosion are indicated in Fig. 8 for the samples in 10% NaCl electrolyte, with and without the inhibitor $BaCrO_4$. The corrosion data further indicate that the Melmag alloy is the more active and corrodes more completely in a shorter time span. However, since the Dow alloy appears to corrode much slower, it would probably be more applicable to a multiple reserve battery application than the Melmag alloy. Furthermore, even these corrosion data do not give favorable indications for magnesium, in general, for a multiple reserve battery system. The corrosion rate was determined by the collection of H_2 gas that resulted from the direct reaction of the magnesium sheet (0.015 inch thick) with excess electrolyte solution.

Figures 9 and 10 show the continuous discharge curves of cells constructed with each of the two alloys. The voltage drop-off is a result of the diminishing surface area due to the build-up of $Mg(OH)_2$ as the magnesium is consumed in the discharge process. From a capacity standpoint, the Dow alloy proved to be the more efficient of the two. On discharge, the Dow alloy delivered 40% of its theoretical capacity while the Melmag alloy produced only 35% of its theoretical capacity.

3.4.3 IRON-OXYGEN TEST CELLS

The process developed for preparing iron oxide for use as an iron electrode was based on the reduction of ferric oxide (Fe_2O_3) to iron in a

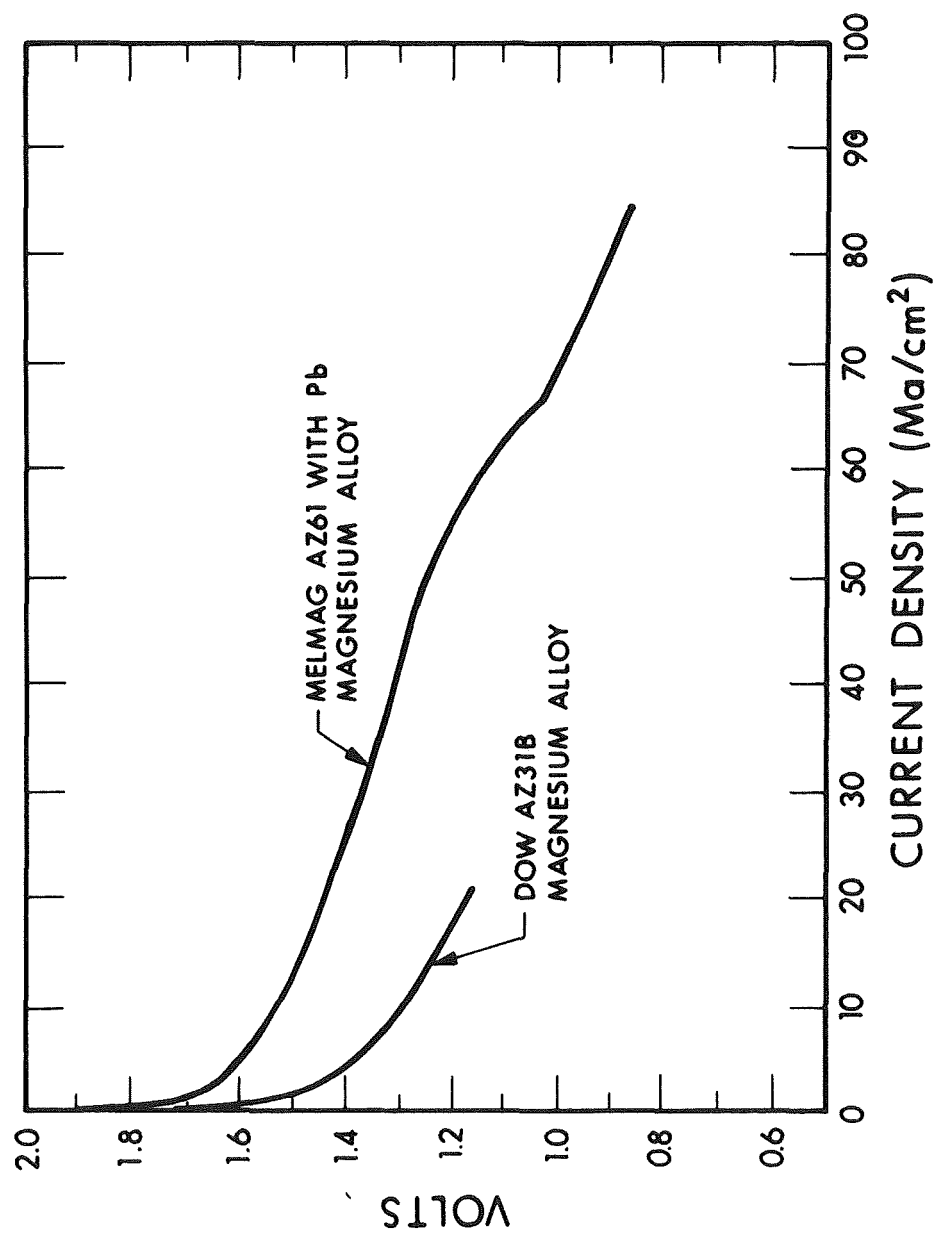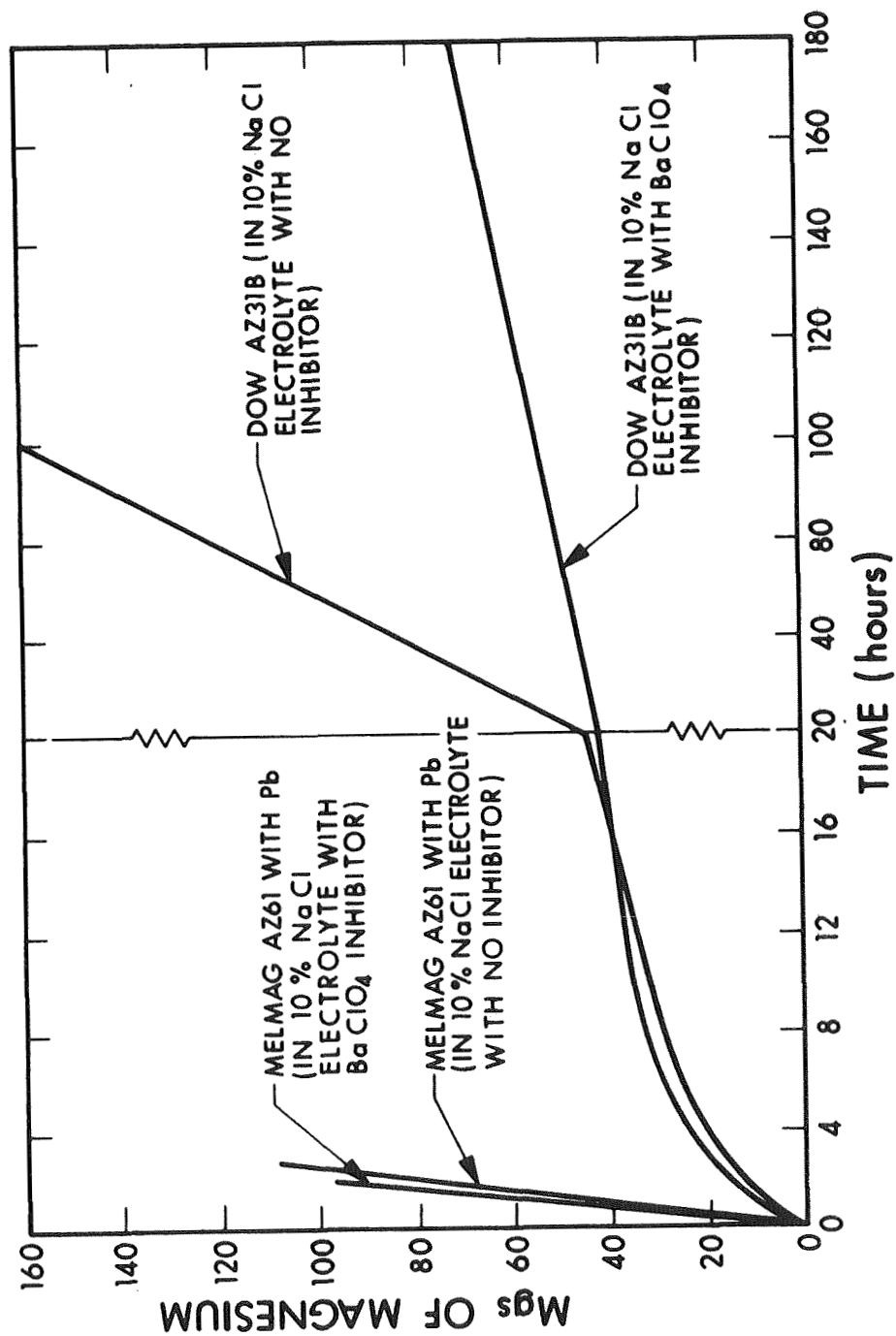Figure 7. Mg-O_2 Polarization Curves

4008-Final

20

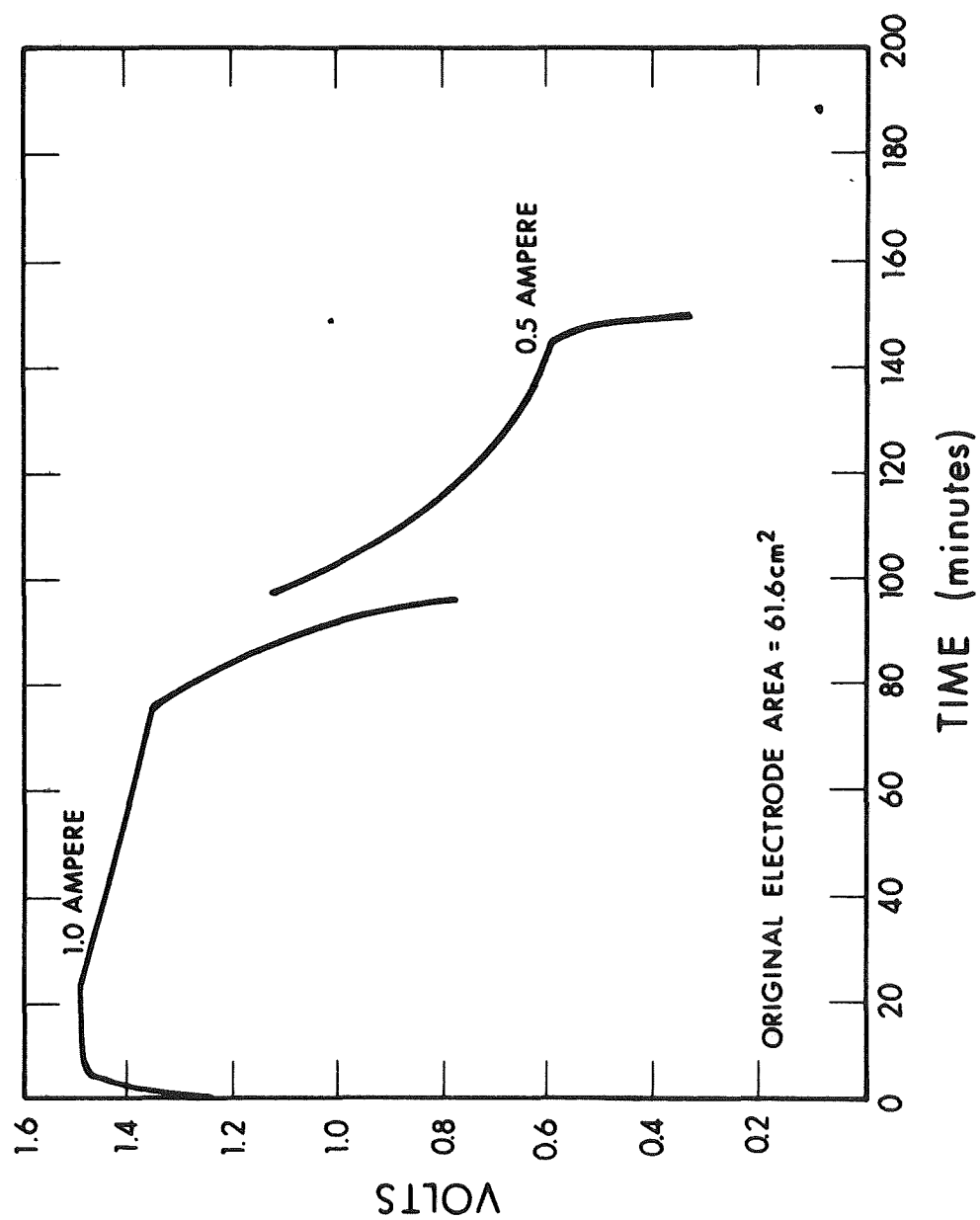Figure 8. Corrosion Rates for Two Magnesium Alloys

31357

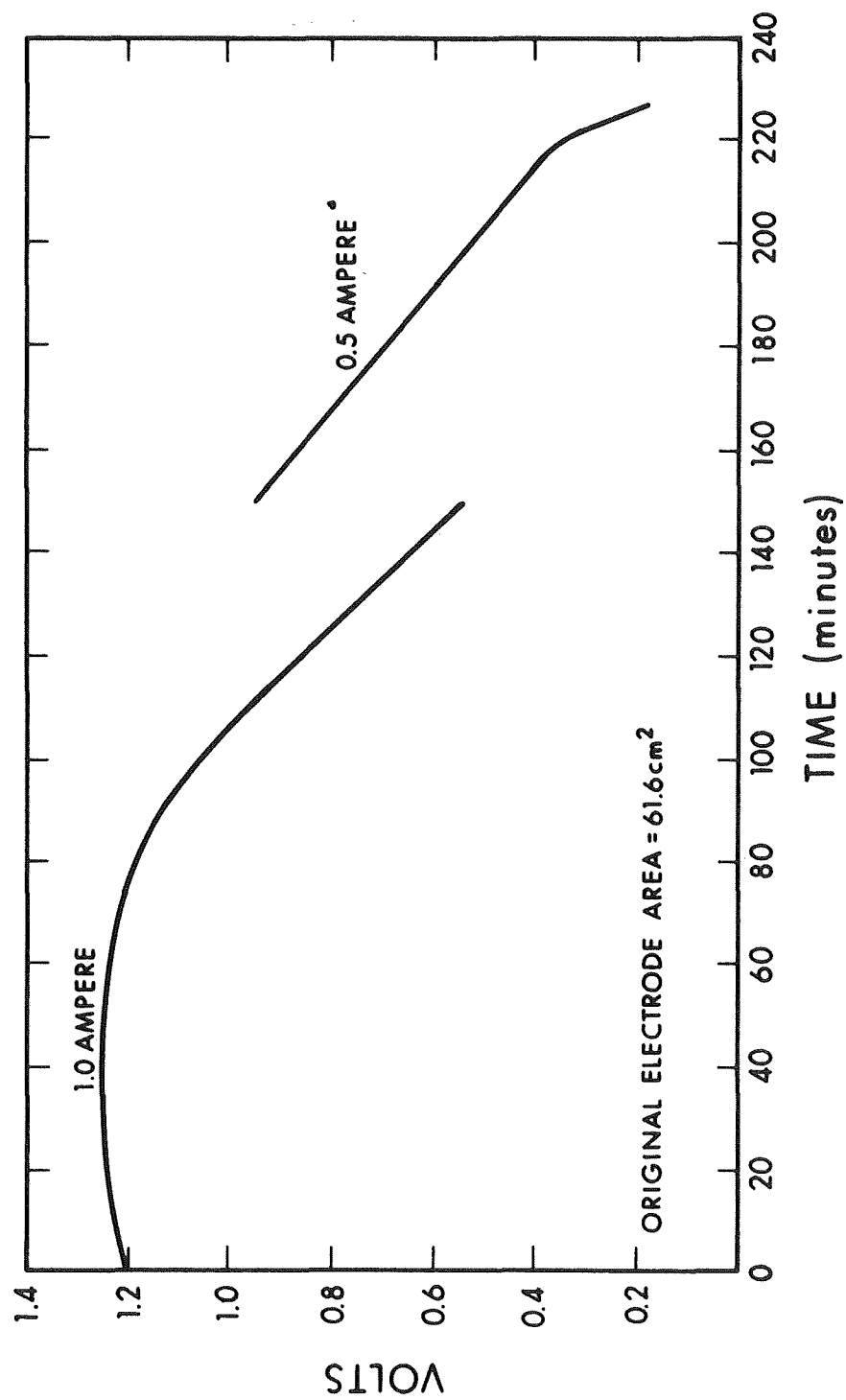Figure 9. Mg-O_2 Continuous Discharge (Melmag AZ61 with Pb)

Figure 10. Mg-O$_2$ Continuous Discharge (Dow AZ 31b)

31359

hydrogen furnace. Since efforts to reduce various oxides to iron electrolytically were less fruitful than desired, the hydrogen furnace method of reduction was used as an alternative. The reduction procedure consisted of heating the Fe_2O_3 to a temperature of approximately 400°C for about 2 hours and then placing the material directly in water to minimize oxidation from exposure to air. After placing the reduced oxide in a water bath, mercuric oxide (5%) was added to the electrode composition. These iron electrodes were tested with nickel electrodes in a manner similar to that in which the cadmium electrodes were tested early in the contract period. Test data (see Fig. 11), shows that on continuous discharge, the iron electrode has a slightly higher initial voltage but does not maintain its output over as long a time period as the cadmium electrode. Test cells were only capable of yielding approximately 1 A-h per 4 grams of active material or about 25% of the theoretical capacity.

3.5 MONOBLOCK CONSTRUCTION

A six-cell monoblock was constructed using cadmium oxide as the metallic electrode. Although there were several reasons for perferring of this battery couple over the magnesium-oxygen and iron-oxygen systems as listed in the conclusions and evalution section, two reasons were overriding. First of all, the magnesium-oxygen system is more applicable for a primary battery in which the requirements are for a continuous discharge. This is true because the magnesium electrode corrodes continuously in the electrolyte until the metal is almost completely consumed. Second, the iron electrode construction procedures could not be used in an efficient manner because any exposure to the outside air following the reduction process would be harmful to the electrode's performance. According to the accumulated test data, the cadmium-oxygen system appears to be the one most adaptable to a multiple reserve application.
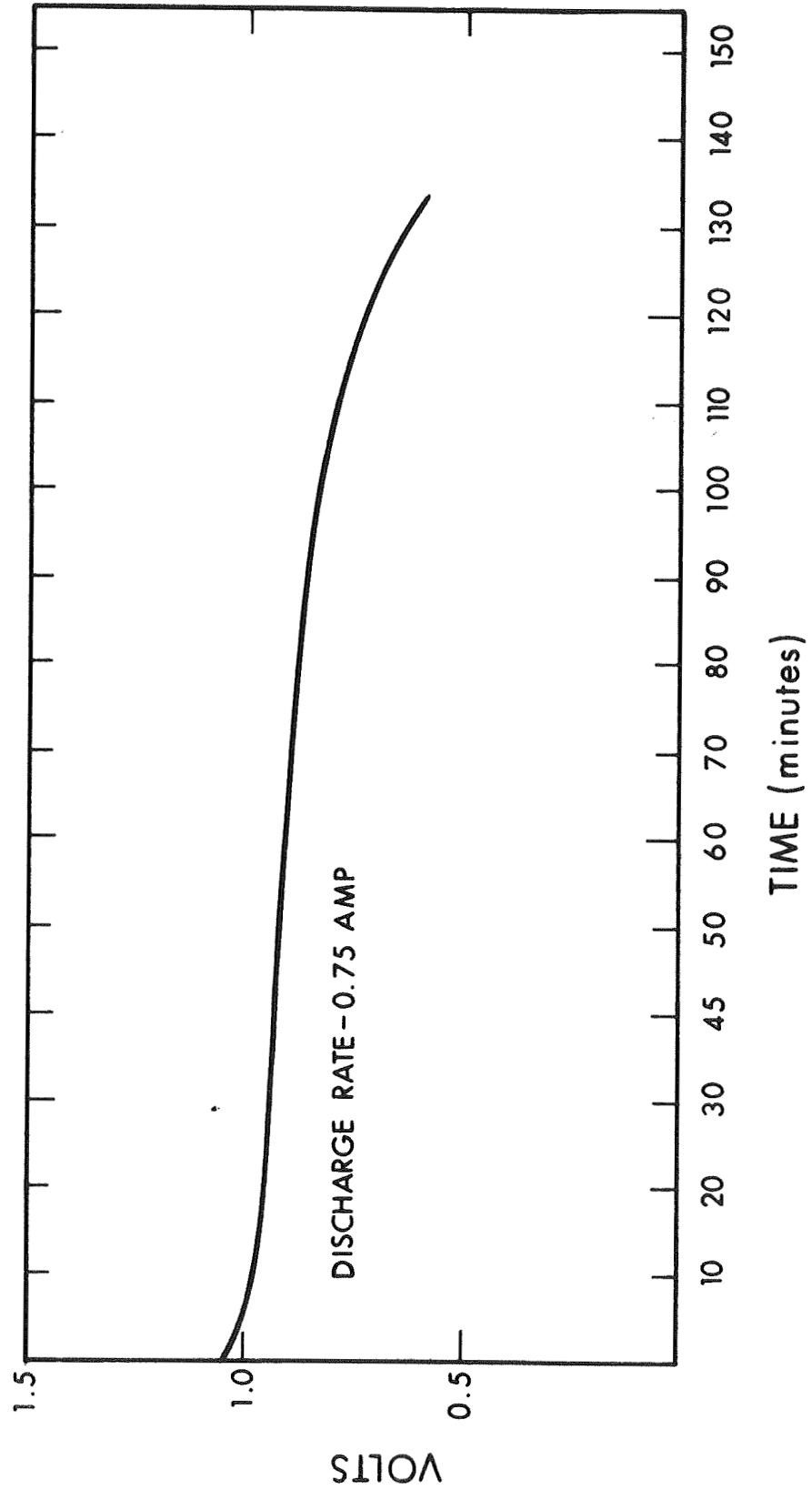
Figure 11. Typical Iron Electrode Discharge Mode

31715

Dimensionally, the monoblock measures 2 3/4 x 3 5/16 x 3 11/16 inches and weighs 1.23 pounds. The structure is very similar to Fig. 1 with one oxygen manifold located near the top of the monoblock body. For test purposes, an oxygen source was attached to the oxygen manifold. The real situation would employ an oxygen storage vessel with an oxygen regulator, as will be described in engineering and design, Section 4. The case for the monoblock was constructed of a series of connected plastic cases similar to the single cell design illustrated in Fig. 4. These cases were glued together to form a single gas-tight unit, and the manifold was then added.

Some positive advantages of the cadmium-oxygen system include the ease of cadmium plate construction, the capability of a feasible on/off power control, the stability of cadmium in KOH electrolyte, and the ease of plate formation. With these advantages in mind, a six-cell 5-volt monoblock was constructed. Test data for this system are shown in Fig. 12.
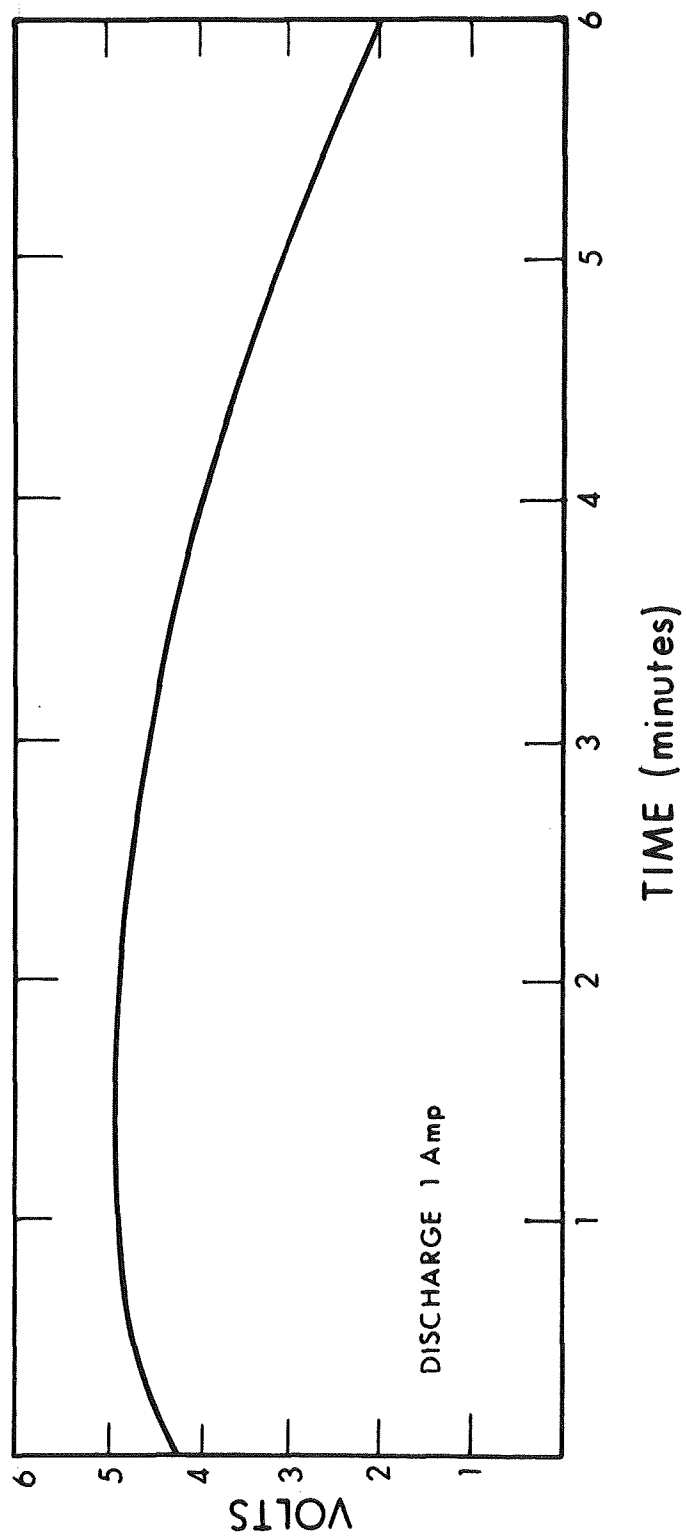
Figure 12. Cd-O$_2$ Six-Cell Monoblock Test

31996

SECTION 4

ENGINEERING DESIGN AND ANALYSIS

4.1 MONOBLOCK DESIGN

To gain a better insight into and understanding of what a complete battery
system would look like, a preliminary engineering analysis was con-
ducted on the cadmium-oxygen and magnesium-oxygen systems. For com-
parison purposes, each system was designed for a 28V rating, and for
10 A-h, 50 A-h, and 100 A-h. The design concept employed was that
which is shown in Fig. 1 and consists of a 31 series-connected cell
block for the $Cd-O_2$ system and a 19 series-connected cell block for
the $Mg-O_2$ system. Since the iron-oxygen system still needs additional
development before it would be a comparable couple for a multiple re-
serve battery application, an engineering analysis for this couple was
not conducted.

Based on the results of Section 3, projected improvements, weight re-
ductions, and weight breakdown estimates for the $Cd-O_2$ and $Mg-O_2$ couples
were prepared. Table II shows the results of the $Cd-O_2$ systems, and
Table III shows the results of the $Mg-O_2$ systems.

4.2 MULTICELL OXYGEN TANKAGE DESIGN

For any of the metal-oxygen primary batteries, a pressurizing oxygen
storage tank is required that should have minimum weight. The quantity
of oxygen required is a direct function of the watt-hour rating of the
battery. For the oxygen systems, the weight of oxygen is determined
by the following:

$$\text{Weight } O_2 \text{ gas} = 1.1 \text{ W-h} \left[\frac{0.298 \text{ gm } O_2}{\text{A-h}} \right] \frac{0.9 \text{ volts}}{\text{Cd cell}} \text{ or } \frac{1.45 \text{ volts}}{\text{Mg cell}}$$

TABLE II

CADMIUM-OXYGEN BATTERY DESIGN

Phase I

Basis: 10 A-h, 28V, 280 W-h

Discharge over 5 hour period: 2A

Active plate area: 16 $in.^2$ = 103 cm^2, electrode thickness = 0.030 inch

Operating voltage per cell: 0.90V, number of cells = 28V/0.90V $\approx$ 31

Single cell design: 4 (2 x 2 inches) CdO plates

Cadmium 10 A-h x 2.1 gm/A-h		21.0 gm Cd/cell
85% utilization		24.7 gm Cd/cell
128.41 M Wt CdO (24.7 gm Cd)		
112.41 M Wt Cd		28.21 gm CdO/cell
5% additives		29.70 gm CdO/cell
Oxygen electrode, 0.4 $gm/in.^2$ x 16 $in.^2$		6.4 gm
Gas diffusion screen, 0.2 $gm/in.^2$ x 16 $in.^2$		3.2 gm
(4) separator (2.25 x 2.25 inches) 0.4 gm		8.0 gm
(2) nickel foil current collector (2.5 x 2.5 inches)		3.6 gm
(4) rubber frame		5.8 gm
Plastic cell case (dual unit), 5/8 inch depth		21.5 gm
Electrolyte		_30.0_ gm
		108.20 gm

Multicell unit: 31 cells x 108.20 gm (-1 case unit)	3340 gm
(32) intercell connectors 5.5 gm x 32	176 gm
Manifold	12 gm
(2) end plates	_12_ gm
Total Stack Weight	3540 gm

W-h/lb (stack) = 280 W-h/7.8 lb = 36 W-h/lb

TABLE II

CADMIUM-OXYGEN BATTERY DESIGN (contd)

Phase II

Basis: 50 A-h, 28V, 1400 W-h

Discharge over 5 hour period: 10A

Active plate area: 80 in^2 = 515 cm^2, electrode thickness = 0.030 inch

Operating voltage per cell: 0.90V, number of cells = 28V/0.90V $\approx$ 31

Single cell design: 4 (4 x 5 inches) CdO plates

Cadmium 50 A-h x 2.1 gm/A-h	105.0 gm Cd/cell
85% utilization	123.5 gm Cd/cell
<u>128.51 M Wt CdO</u> (123.5 gm Cd)	
112.41 M Wt Cd	141.0 gm CdO/cell
5% additives	148.5 gm
Oxygen electrode, 0.4 gm/in^2 x 80 in^2	32.0 gm
Gas diffusion screen, 0.2 gm/in^2 x 80 in^2	16.0 gm
(4) separator (5 x 4 inches), 0.4 gm/in^2 x 80 in^2	32.0 gm
(2) nickel foil current collector (5.125 x 4.125 inches), 0.3 gm/in^2 x 42.25 in^2	12.7 gm
(4) rubber frame (1/8 inch strip), 0.125 gm/in. x 72 in.	9.0 gm
Electrolyte	150.0 gm
Plastic cell case (9/16 x 5 x 5 inches)	<u>40.0</u> gm
	440.2 gm

Multicell unit: 31 cells x 440.2 gm (-1 case unit)	13374 gm
(32) intercell connectors 5.5 gm x 32	176 gm
Manifold	15 gm
(2) end plates	<u>25</u> gm
	13590 gm
Total Stack Weight	30 lb

W-h/lb (stack) = 1400 W-h/30 lb = 46.7 W-h/lb

TABLE II

CADMIUM-OXYGEN BATTERY DESIGN (contd)

Phase III

Basis: 100 A-h, 28V, 2800 W-h

Discharge over 5 hour period: 20A

Active plate area 160 in^2, electrode thickness = 0.030 inch

Operating voltage per cell: 0.90V, number of cells = 28V/0.90V $\approx$ 31

Single cell design: 8 (4 x 5 inches) CdO plate

Cadmium 100 A-h/cell	282.1	gm CdO/cell
5% additives	297.0	gm
Oxygen electrode 0.4 gm/in^2 x 160 in^2	64.0	gm
Gas diffusion screen 0.2 gm/in^2 x 160	32.0	gm
(8) separator (5 x 4 inches) 0.4 gm/in^2 x 160 in^2	64.0	gm
(4) nickel foil current collector (5.125 x 4.125 inches) 0.3 gm/in^2	25.4	gm
(8) rubber frames 1/8 inch strip 0.125 gm/in. x 144 in.	18.0	gm
Electrolyte	300.0	gm
Plastic cell case (9/8 x 5 x 5 inches)	50.0	gm
	850.4	gm

Multicell unit: 31 cells x 850.4 (-1 case unit)	26,312	gm
(32) intercell connectors 5.5 gm x 32	176	gm
Manifold	30	gm
(2) end plates	25	gm
Total Stack Weight	26,543	gm
	57.5	lb

W-h/lb (stack) = 2800 W-h/58.5 lb = 49 W-h/lb

TABLE III

MAGNESIUM-OXYGEN BATTERY DESIGN

Phase I

Discharge over 5 hour period: 2A

Basis: 10 A-h, 28V, 280 W-h

Active plate area: 28.5 in^2 (both sides of 14.25 in^2 Mg alloy)

Operating voltage per cell: 1.45V, number of cells = 28V/1.45V $\approx$ 19

Single cell design: 3 (2.5 x 2.5 inches) Mg alloy, thickness = 0.015 inch

(3) magnesium alloy 10 A-h required	9.45 gm Mg alloy/cell	
Assuming 3.5 A-h/9.5 in^2 or 3.5 A-h/3.1556 gm		
(6) oxygen electrode (2.5 x 2.5 inches), 0.4 gm/in^2 x 37.5 in^2	15.0	gm
(7) gas diffusion screen (2.5 x 2.5 inches) 0.2 gm/in^2 x 43.7 in^2	8.7	gm
(6) separator (2.5 x 2.5 inches), 0.4 gm/in^2 x 37.5 in^2	15.0	gm
Plastic cell case (0.35 x 2.75 x 3.25 inches)	20.0	gm
Electrolyte	30.0	gm
	98.15	gm

Multicell unit: 19 cells x 98.15 gm (-1 case unit)	1865	gm
(20) intercell connector 20 x 5.5 gm	110	gm
Manifold	10	gm
(2) end plates	25	gm
Total Stack Weight	2010	gm
	4.43	lb

W-h/lb (stack) = 280 W-h/4.43 lb = 63 W-h/lb

TABLE III

MAGNESIUM-OXYGEN BATTERY DESIGN (contd)

<u>Phase II</u>

Basis: 50 A-h, 28V, 1400 W-h

Discharge over 5 hour period: 10A

Active plate area: 142.5 in^2 (both sides of 71.25 in^2 Mg alloy)

Operating voltage per cell: 1.45V, number of cells = 28V/1.45V $\approx$ 19

Single cell design: 2 (6 x 6 inches) Mg alloy, thickness = 0.015 inch

(2) magnesium alloy 50 A-h requires	47.25
Assuming 3.5 A-h/9.5 in^2 or 3.5 A-h/3.1556 gm	
(4) oxygen electrodes (6 x 6 inches), 0.4 gm/in^2 x 144 in^2	57.5 gm
(5) gas diffusion screen (6 x 6 inches), 0.4 gm/in^2 x 180	32.4 gm
(4) separator (6 x 6 inches), 0.4 gm/in^2 x 144 in^2	57.5 gm
Plastic cell case (0.35 x 6.25 x 6.5 inches)	30.0 gm
Electrolyte	<u>150.0</u> gm
	374.65 gm

Multicell unit: 19 cells x 374.65 (-1 case unit)	7100 gm
Intercell connectors	110 gm
Manifold	20 gm
End plates	<u>40</u> gm
Total Stack Weight	7270 gm

W-h/lb (stack) = 1400 W-h/16.1 lb = 87 W-h/lb

TABLE III

MAGNESIUM-OXYGEN BATTERY DESIGN (contd)

Phase III

Basis: 100 A-h, 28V, 2800 W-h

Discharge over 5 hour period: 20A

Active plate area: 285 in^2 (both sides of 142.5 in^2 Mg alloy)

Operating voltage per cell: 1.45V, number of cells = 28V/1.45V $\approx$ 19

Single cell design: 4 (6 x 6 inches) Mg alloy, thickness = 0.015 inch

(4) magnesium alloy 100 A-h requires	94.5 gm Mg alloy/cell
Assuming 3.5 A-h/9.5 in^2 or 3.5 A-h/3.1556 gm	
(8) oxygen electrode (6 x 6 inches), 0.4 gm/in^2 x 324 in^2 x 288 in^2	115.0 gm
(9) gas diffusion screen (6 x 6 inches), 0.2 gm/in^2 x 324 in^2	64.8 gm
(8) separator (6 x 6 inches), 0.4 gm/in^2 x 288 in^2	115.0 gm
Plastic cell case (0.7 x 5.25 x 5.25 inches)	40.0 gm
Electrolyte	300.0 gm
	729.3 gm

Multicell unit: 19 cells x 729.3 gm (-1 cell case)	13250 gm
Intercell connector	110 gm
Manifold	40 gm
End plates	40 gm
Total Weight	13440 gm
	29.6 lb

W-h/lb (stack) = 2800 W-h/29.6 lb = 94.5 W-h/lb

Figure 13 shows the weight of oxygen for batteries, assuming 1.45V/cell for Mg and 0.9 volt per cell for Cd at the operating voltage. The 1.1 factor allows for a 10% oxygen excess. To optimize the tankage weight, compressibility pressure relationships are required.

Figure 14 shows physical property data of oxygen density as a function of pressure at 70°F. At pressures in the 4,000 to 10,000 psi range, the gas deviates from the ideal gas law as shown in Fig. 14.

Tankage volume as a function of battery watt-hour and gas storage pressure is shown in Fig. 15. The tankage weight of a sphere can be calculated from the thin wall pressure vessel relationship as follows:

$$\sigma = \frac{PR}{2t}$$

$$w = 4\pi R^2 t \gamma$$

$$V = (4/3) \pi R^3$$

Therefore $w = 3PV\gamma/2\sigma$

Where t = wall thickness

P = pressure

R = sphere radius

σ = allowable stress

V = volume

γ = tank material density

W = tank weight

The material of the tank and its strength-to-weight ratio are the key criteria. Two classes of high-strength-to-weight materials are available. The first class of high-strength materials includes aluminum, nickel, and steel while the second class consists of filament-wound materials.
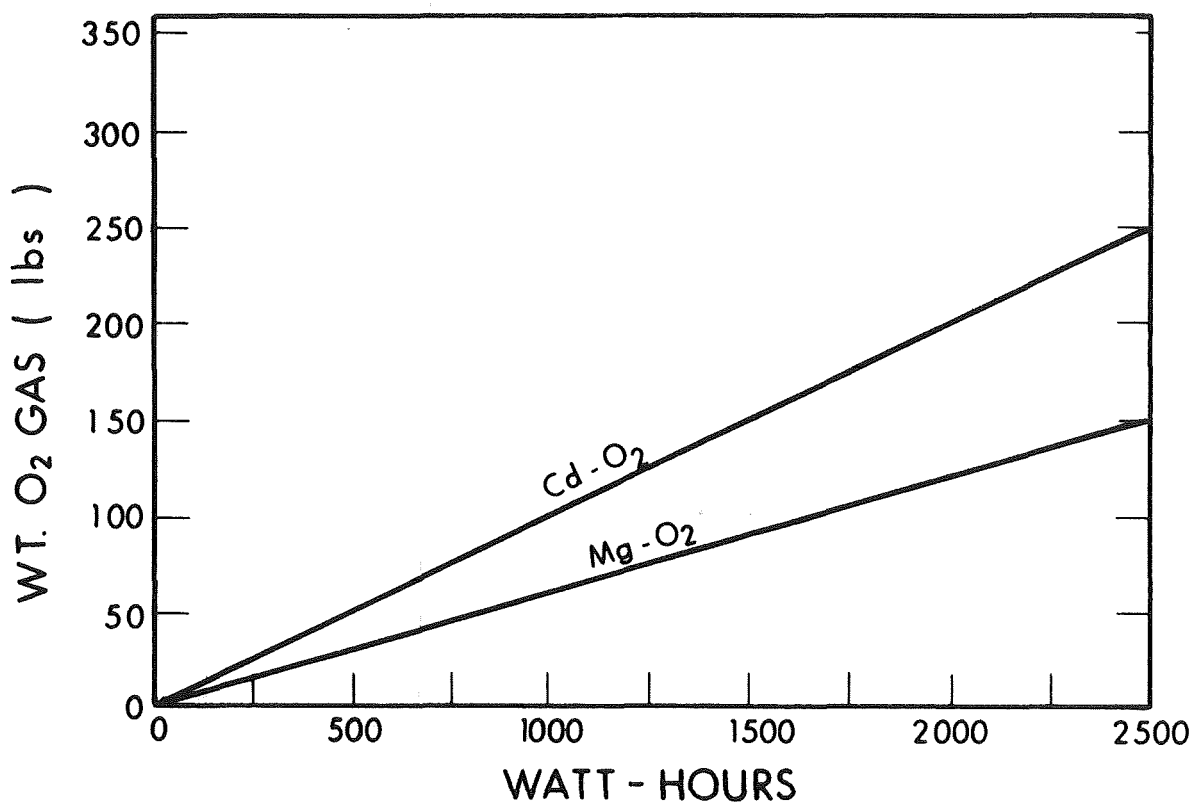
Figure 13. O_2 Weight for Cd-O_2 and Mg-O_2 as a Function of Battery Watt-Hours
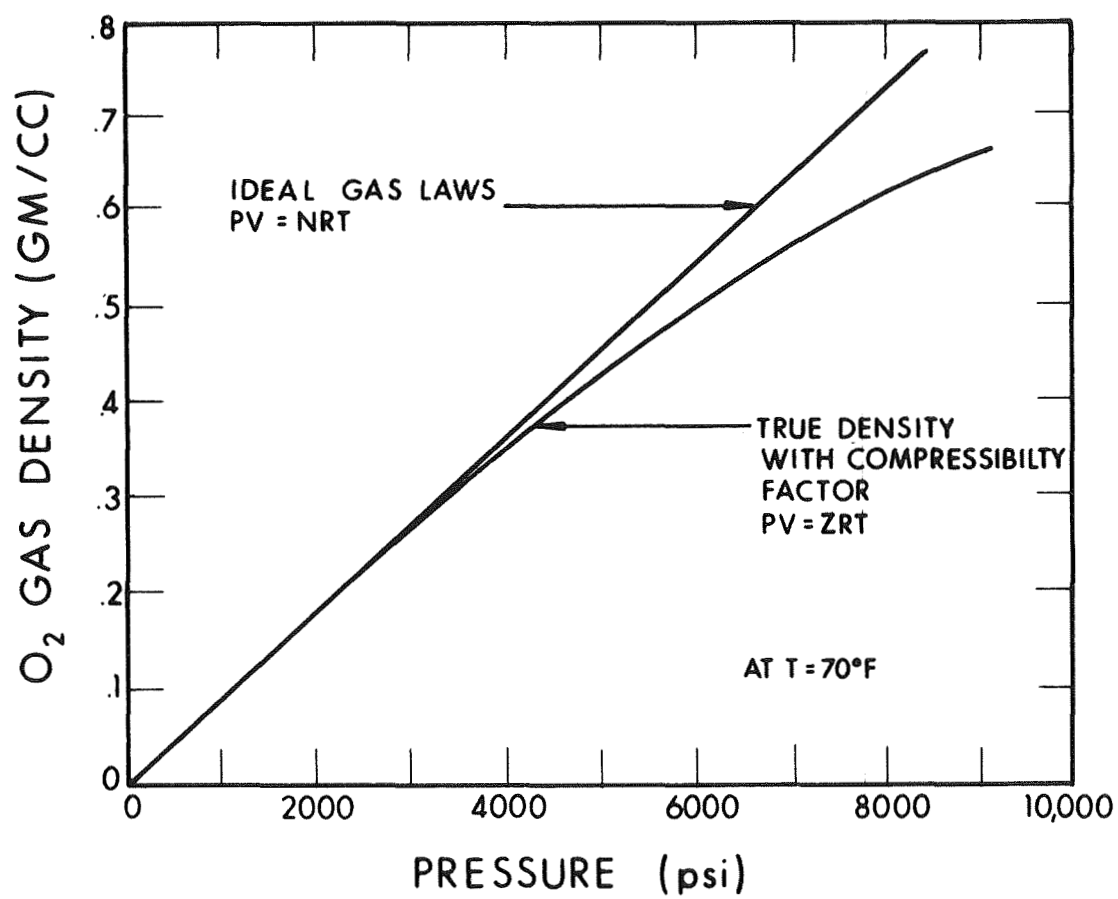
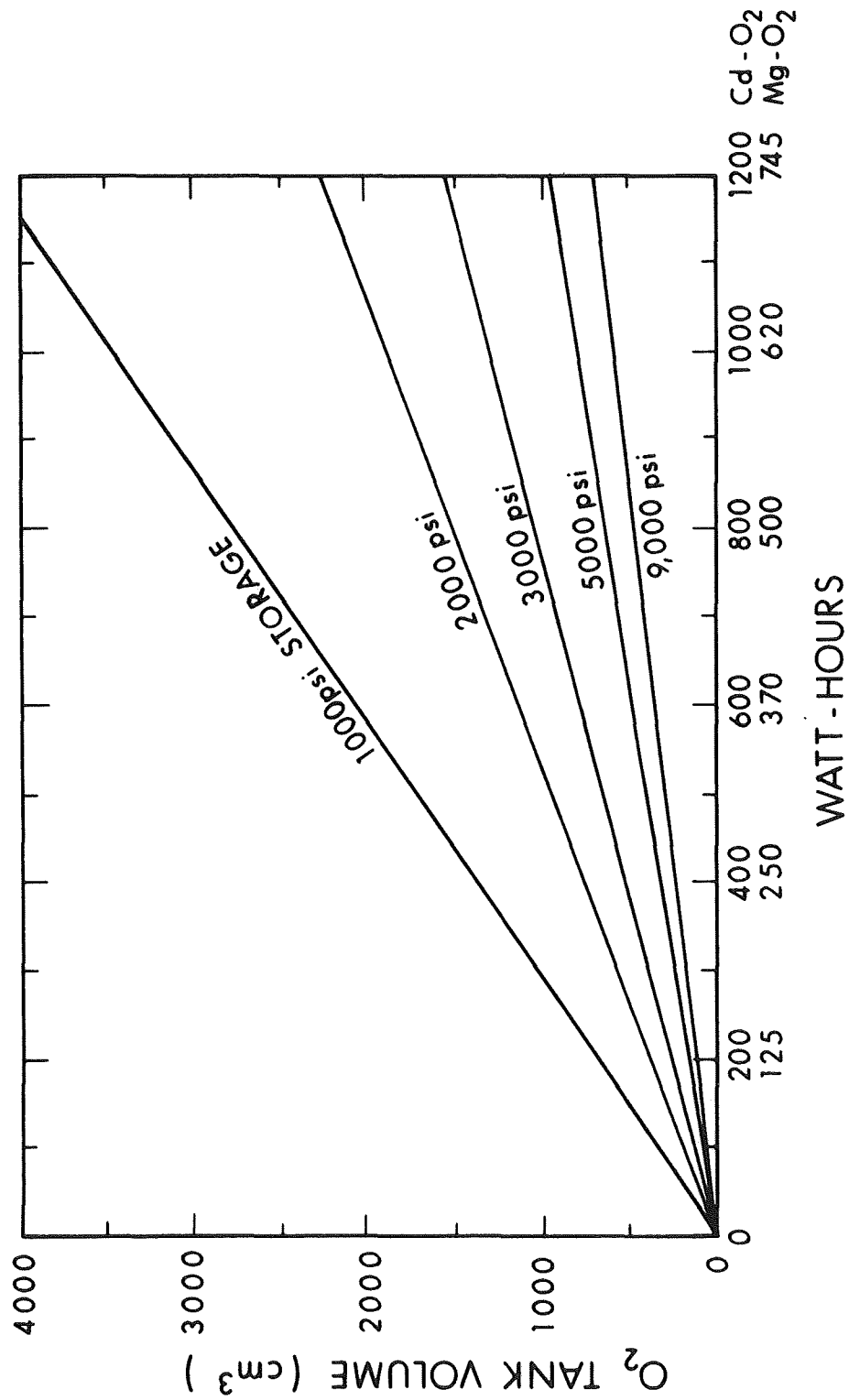Figure 14. Oxygen Density as a Function of Pressure

Figure 15. Oxygen Tank Volume as a Function of Watt-Hours and Storage Pressure

31096

Table IV lists the various tank materials available and their physical properties (Ref. 4). Figure 16 shows the relationship of storage pressure to the tank reactant weight for the different materials.

The conclusions reached are that a vessel having a tankage-to-reactant weight ratio of 1 to 1 is attainable with the first class of materials, and the filament-wound vessels are capable of a 0.5 weight ratio of tankage-to-reactant. As a result of the nonlinearity of the oxygen compressibility, the optimum oxygen pressure is approximately 2500 psi.

TABLE IV

TANK MATERIAL

Material	Stress/Density (in. x 10^6)
Glass filament wound SS or Al liners	1.7 - 2.2
Titanium 6 Al-4V	1.0
Stainless Steel 301	0.75
Inconel 718	0.65
Aluminum 6 Al-4V	0.65

4.3 BATTERY SYSTEM WEIGHT

From the results of Subsection 4.1 and 4.2, the complete battery weight breakdown is summarized in Table V and graphically presented in Fig. 17.

The O_2 tank weight was taken on a 1 to 1 weight ratio. Inquiries were made from various pressure regulator manufacturers, and responses showed that regulators from 3/4 lb to 2 lb are available to take a 2000 to 3000 psi input and feed 15 psi. The gas flow rate is assumed to be relatively slow, and a constant 0.8 lb was taken for the regulator in all cases.
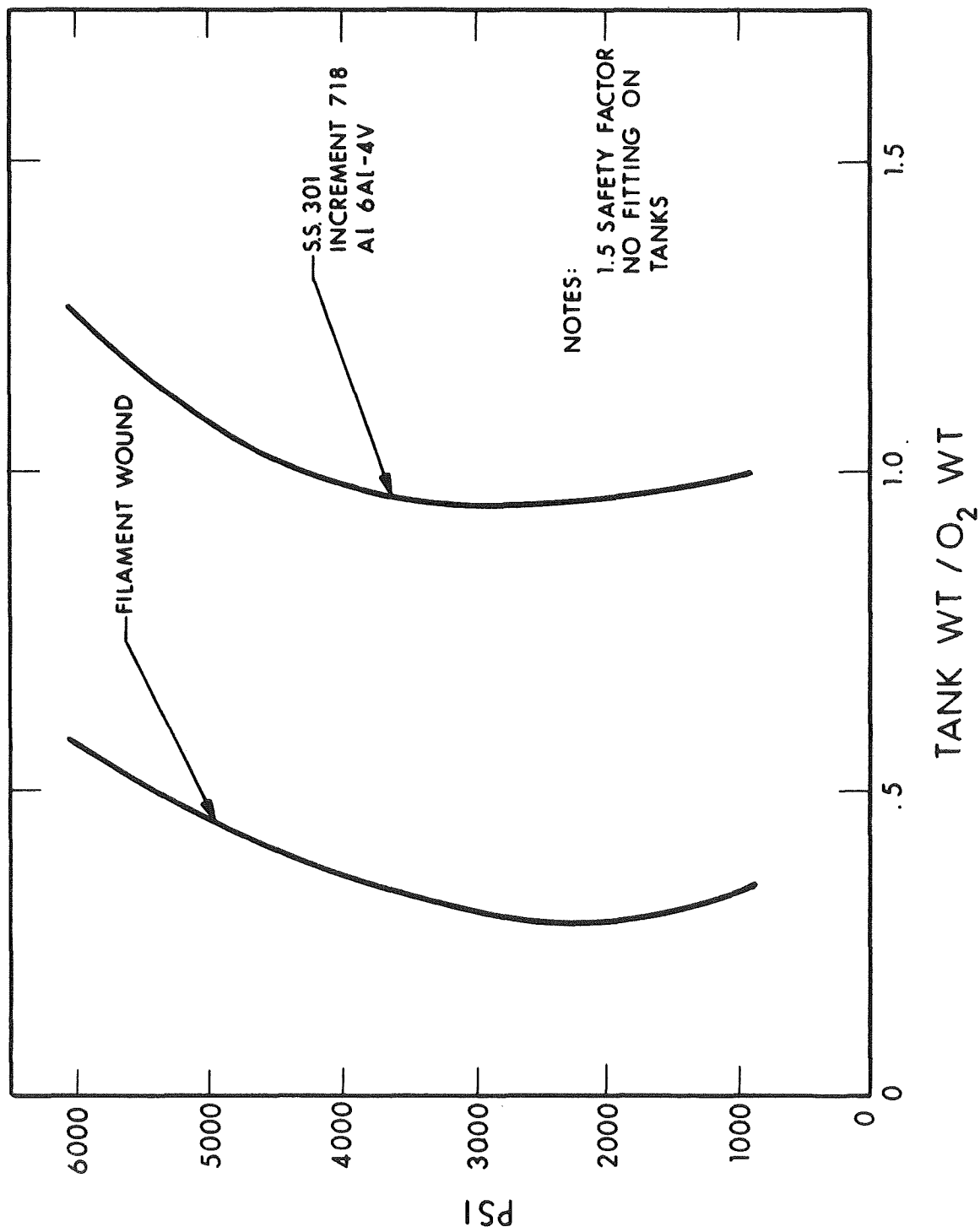
Figure 16. Tank/O$_2$ Weight versus O$_2$ Pressure

31998

TABLE V

BATTERY SYSTEMS WEIGHT SUMMARY

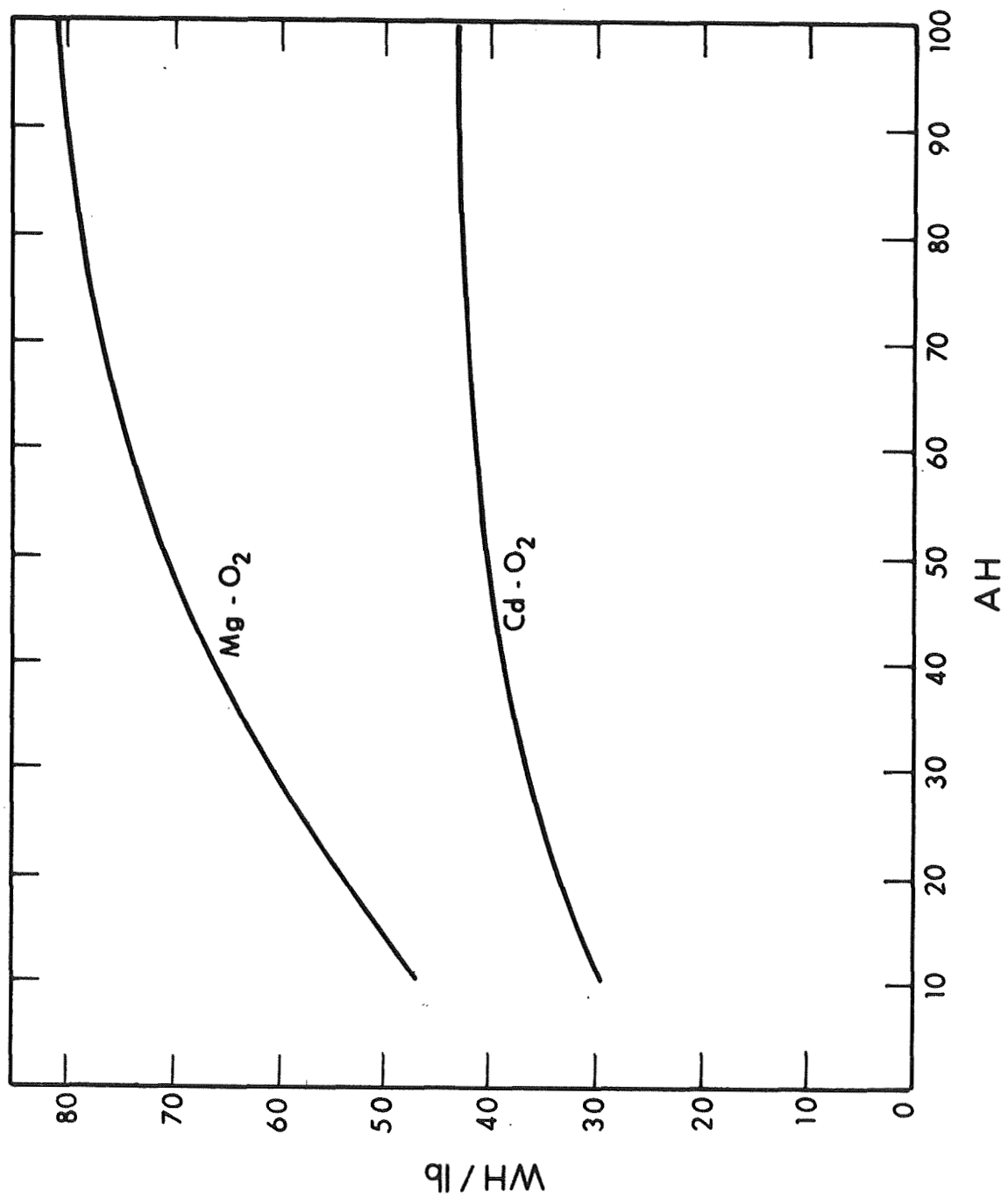| A-h	W-h	Stack Wt(lbs)	Stack W-h/lb	O_2 Wt. (lbs)	O_2 Tank (lbs)	O_2 Reg. Mis.	Total Wt(lbs)	Total W-h/lb
				$Cd-O_2$				
10	280	7.8	36	.22	.22	.8.5	9.5	29.5
50	1400	30.0	47	1.1	1.1	.81.0	34.0	41.0
100	2800	57.5	49 50	2.2	2.2	.81.5	64.2	43.5
				$Mg-O_2$				
10	280	4.43	63	.130	.136	.8.5	6.0	47
50	1400	16.1	87	.68	.68	.81.0	19.3	72.5
100	2800	29.6	94.5	1.37	1.37	.81.5	34.7	81

Figure 17. Energy Density of Multiple Reserve Metal-O_2 Systems

31997

REFERENCES

1. M. Klein and R. Astrin, Hydrogen-Oxygen Electrolytic Regenerative Fuel Cells, Final Report Contract NAS3-2781 (1968)

2. P. L. Howard and F. Solomon, Silver Oxide Secondary Batteries, 13th Power Sources Conference (1959), pp. 92 to 96

3. M. Eisenberg and M. Klein, Long Wet Shelf Primary Battery, Electrochem. Tech. Vol 3, No. 1-2, pp. 58 to 60

4. E. Morris, The Performance of Glass Filament Wound Pressure Vessels with Metal Liners, Proceedings of 17th ASTM Meeting